

LIQUID JUNCTION POTENTIALS
I. REPRODUCIBLE STATIC LIQUID JUNCTIONS
CONSTANT IN POTENTIAL OVER LONG
PERIODS OF TIME

LIQUID JUNCTION POTENTIALS
II. A DIRECT COMPARISON OF STATIC AND
FLOWING JUNCTIONS

HIGH-PRECISION CONSTANT-TEMPERATURE
BATH

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the University of Michigan

By
KENNETH VAN LENTE
1931

Allen Arbor

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The author wishes to express his thanks to Dr. A. L. Ferguson, under whose supervision this work was done, and also to Mr. R. M. Hitchens for his interest and suggestions.



[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

LIQUID JUNCTION POTENTIALS. I. REPRODUCIBLE STATIC LIQUID JUNCTIONS CONSTANT IN POTENTIAL OVER LONG PERIODS OF TIME¹

BY ALFRED L. FERGUSON, KENNETH VAN LENTE AND RICHARD HITCHENS

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Static liquid junctions have caused endless difficulties since measurements of single electrode and concentration cell potentials were first attempted.² To get results at all reproducible, investigators have adopted numerous arbitrary methods for overcoming these difficulties, but none are accepted as satisfactory. Such procedures, of course, have rendered the data empirical.³ An extensive study of the most promising devices was made by Lamb and Larson.⁴ They concluded that results with static junctions, made in various ways, are unsatisfactory, and, therefore, proceeded to develop the flowing junction.

There are many instances, however, where it is not possible or convenient to use flowing junctions and yet it is highly important that constant and reproducible values be obtained; for instance, in the comparison of the standard hydrogen with a calomel or any other electrode, liquid junction potential is included in the measurement and becomes a part of the value given to the calomel or other electrode. All such values are as uncertain as the boundary potential, and whenever the calomel electrode is used as a standard the assumption must be made that the solution potential, which is a part of its value, always remains the same. When a saturated calomel electrode or a bridge of saturated potassium chloride is used, the common assumption is that no boundary potential exists under these conditions. It is well known, however, that neither of these assumptions is justified. The present work is an attempt to construct static boundaries of this nature in such a manner as to give potentials more constant and reproducible than have previously been done. The

¹ The material in this article is from a portion of the thesis submitted to the Graduate School of the University of Michigan by Kenneth Van Lente in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² The present authors do not include a bibliography because several are now in print; see, for instance, Guggenheim, *THIS JOURNAL*, 52, 1315 (1930).

³ These remarks do not apply to junctions which consist of two different concentrations of the same electrolyte. Such boundaries, according to both theory and practice, give but little trouble.

⁴ Lamb and Larson, *THIS JOURNAL*, 42, 229 (1920).

systems used were selected because of their importance in connection with the determination of the relative values of calomel electrodes and because saturated calomel electrodes, or other calomel electrodes in conjunction with a saturated potassium chloride bridge, are so extensively used in *PH* measurements.

Most valuable contributions, both theoretical and experimental, to this field have been made recently by MacLagan, Bjerrum, Guggenheim and their co-workers.^{5,2} Some of the systems used by these investigators are similar to those herein described. Unmack and Guggenheim, in their last article on this topic, introduced several improvements upon their earlier works, but still they state the tenth normal calomel electrodes have a probable error of ± 0.15 mv. and the 3.5 normal are "less stable and slightly less reproducible." Concerning the boundary potentials it is stated, "We reduced the erratic fluctuations of the free diffusion measurements from about ± 0.25 mv. to ± 0.1 mv." The saturated calomel electrodes used in the present work showed a maximum variation of 0.05 mv. and remained constant to 0.02 mv. for several months. One of the major factors in this reproducibility and constancy is the maintenance of a constant temperature throughout the whole period. Freshly prepared electrodes required several days in the constant temperature bath before their potentials became stable; and when electrodes were left out of the bath while cells were being reassembled, it required several hours to regain their former value.

Apparatus and Materials

Electrodes.—Several saturated calomel electrodes were used as references. The type was a slight modification of that used by G. N. Lewis.⁶ Much care was exercised in their preparation. The silver chloride electrodes were made by a method closely similar to that recommended by Carmody.⁷ Such electrodes were fairly reproducible and remained constant to within 0.02 mv. for periods of time longer than the cells were measured.

The liquid junction vessels were 9-mm. three-way stopcocks. The stopcocks were placed in such a position that the junctions were horizontal in vertical tubes (see E, Fig. 2). A special stopcock grease, made by heating at 110° a mixture of equal weights of crepe rubber and white vaseline until it became uniform in body, was found necessary to prevent oil from leaking in and liquid from seeping around the stopcock.

Measuring Apparatus.—The potentials were measured on a Leeds and Northrup Type K potentiometer equipped with a Leeds and Northrup 2285-c High Sensitivity galvanometer. The Weston saturated standard cell was calibrated by the Bureau of Standards. Measurements were checked frequently on another potentiometer set-up in the same room and always found to agree within 0.01 mv. The temperature was maintained constant at 25.00° by an electrically controlled oil-bath.

⁵ MacLagan, *Biochem. J.*, **23**, 309 (1929); Unmack and Guggenheim, *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **10**, No. 8 (1930).

⁶ Lewis, Brighton and Sebastian, *THIS JOURNAL*, **39**, 2245 (1917).

⁷ Carmody, *ibid.*, **51**, 2901 (1929).

Solutions.—Extensive precautions were taken to make certain that the potassium chloride solutions were at all times saturated. This is an important factor. The hydrochloric acid solutions were made from redistilled Baker and Adamson c. p. hydrochloric acid. They were analyzed by three gravimetric determinations and the results showed that they were exact for this work.

Experimental

Boundaries were made first in the customary manner by dipping the side arms of two saturated calomel electrodes into a beaker of 0.10 *M*

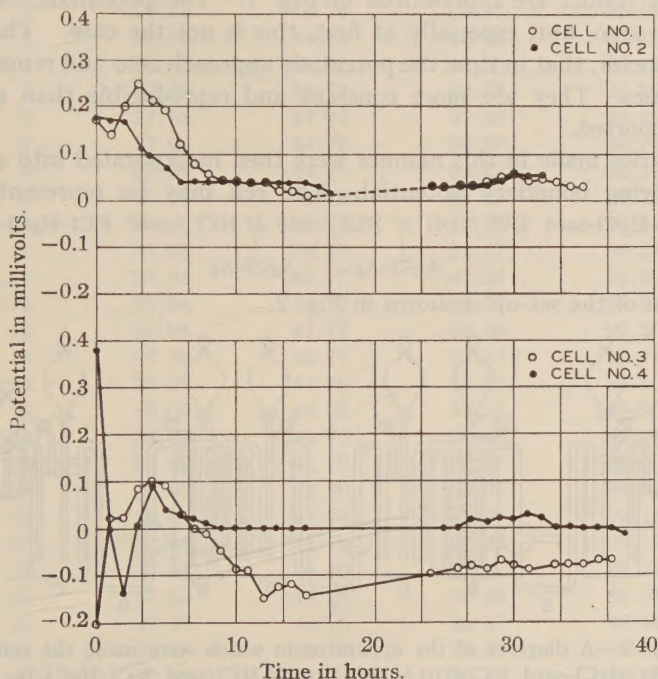
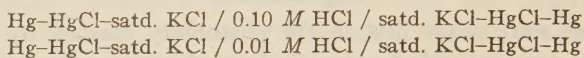


Fig. 1.—Curves showing how the potentials of the cells Hg-HgCl-satd. KCl/0.10 *M* HCl/satd. KCl-HgCl-Hg; Hg-HgCl-satd. KCl/0.01 *M* HCl/satd. KCl-HgCl-Hg varied with time when the junctions were made horizontally in 9-mm. stopcocks.

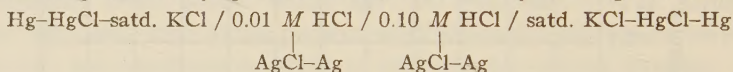
hydrochloric acid. The potentials were neither zero, reproducible nor constant. The nature of the junction was varied in several ways. The electrode side arms with and without constricted tips in some cases were dipped straight down into the acid solution; in others the tips were turned up, and in still others the vertical parts of the tubes were filled with various mixtures of the two solutions so as to produce a more "continuous mixture" boundary. The results showed clearly that cells which contain liquid junctions between saturated potassium chloride and 0.10 *M* hydrochloric acid solutions made by any of these methods are indefinite to the extent of 0.2 mv. or more.

In earlier work in this Laboratory the major boundary under investigation has been made in three-way stopcocks with considerable success. In the present work this system was applied also to the supporting boundaries which are usually made in an indefinite manner. The two following types of cells were used



Typical results are represented in Fig. 1. The potentials, of course, should be zero, but, especially at first, this is not the case. The results show, however, that in time the potentials approach zero and remain so for many hours. They are more constant and reproducible than any previously reported.

Boundaries made in this manner were then incorporated into a typical cell involving boundary potential. The cell may be represented as



A diagram of the set-up is shown in Fig. 2.

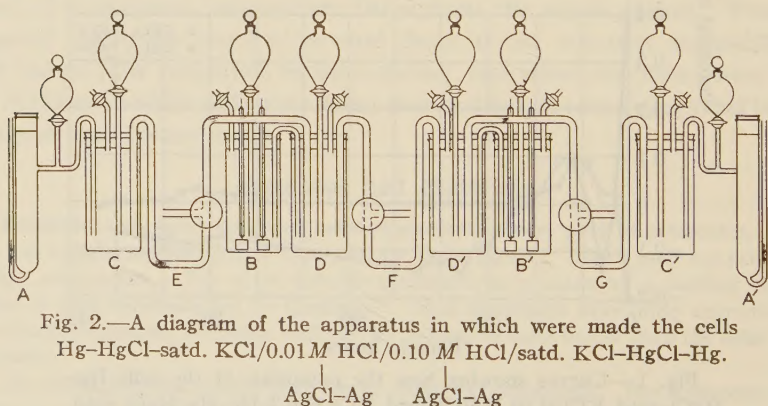
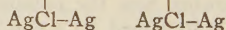


Fig. 2.—A diagram of the apparatus in which were made the cells
Hg-HgCl-satd. KCl/0.01 *M* HCl/0.10 *M* HCl/satd. KCl-HgCl-Hg.



With this arrangement the combined potential of all three boundaries could be determined, and also any variations in individual boundaries.

A typical set of data is given in Table I. The letters above each column correspond to those used to designate the parts of the cell system represented at the head of the table and in Fig. 2, and indicate over what portion of the whole cell system the values in the respective columns apply. The last three columns give data regarding the constancy of the three individual boundaries, G, F, and E, respectively. It is obvious that the individual boundaries are extremely constant in potential. The potential between the two concentrations of hydrochloric acid is as constant as the silver chloride electrodes themselves, which is in complete agreement with past experimental work by many investigators.

TABLE I

A TYPICAL EXAMPLE OF THE RESULTS OBTAINED WITH A CELL OF THE TYPE
 $\text{Hg-HgCl-satd. KCl} / 0.01 \text{ M HCl} / 0.10 \text{ M HCl} / \text{satd. KCl-HgCl-Hg}$

A	AgCl-Ag		AgCl-Ag	
	B	B'	B'	A'
Time, hours	Pot. A-A', mv.	Pot. B'-A', mv.	Pot. B-B', mv.	Pot. A-B, mv.
0	37.99	44.81	92.37	99.19
1	37.97	44.79	92.37	99.19
2	37.95	44.76	92.37	99.18
3	37.95	44.75	92.38	99.18
4	37.93	44.73	92.38	99.18
5	37.92	44.73	92.38	99.19
6	37.93	44.75	92.38	99.20
7	37.92	44.76	92.37	99.21
8	37.93	44.77	92.37	99.21
9	37.93	44.78	92.37	99.22
10	37.92	44.77	92.38	99.22
11	37.93	44.77	92.37	99.21
12	37.94	44.77	92.37	99.20
13	37.94	44.77	92.37	99.20
14	37.94	44.77	92.38	99.20
15	37.98	44.77	92.37	99.17
24	38.07	44.76	92.36	99.06
25	38.09	44.76	92.37	99.06
26	38.09	44.76	92.36	99.05
27	38.07	44.76	92.37	99.06
28	38.07	44.76	92.37	99.07
29	38.00	44.76	92.37	99.14
30	37.96	44.76	92.37	99.17
31	37.93	44.76	92.37	99.21
32	37.93	44.76	92.38	99.21
33	37.97	44.76	92.37	99.17
34	37.98	44.76	92.37	99.16
35	37.99	44.76	92.38	99.15
36	37.98	44.76	92.37	99.15
37	37.99	44.77	92.37	99.15
38	37.99	44.77	92.38	99.15
48	37.99	44.77	92.38	99.15
Av.	37.98	44.76	92.37	99.16
Av. dev.	± 0.04	± 0.01	± 0.00	± 0.04

It should be mentioned that the technique involved in making the assembly is an important factor. After all parts were rigidly located through the use of suitable supports and clamps and the vessels filled with their respective solutions, the boundaries were formed within the large three-way stopcocks. To do this the lower part was filled by suction with the more dense solution, the stopcock was then turned through 180° , the remaining solution drawn out, the stopcock washed several times with

the less dense solution, and finally filled by suction with the less dense solution. It was closed by turning through an angle of 45° . In adjusting the liquid levels, account had to be taken, of course, of the difference in densities of the solutions on opposite sides of the boundary.

The apparatus was left in the thermostat overnight. The next morning the small stopcock in each beaker was opened to ensure atmospheric pressure. The boundaries were then formed by turning the large stopcocks through 45° , and were left undisturbed throughout the experiment. These are true "free diffusion boundaries."

In order to test the reproducibility and constancy over long periods of time of the potentials of this cell system and to establish an accurate value for the so-called boundary potential between 0.1 and 0.01 *N* hydrochloric acid, fifteen cells were measured which were the same as those described above. The results are recorded in Table II. The first column

TABLE II
A SUMMARY OF THE RESULTS OBTAINED WITH FOURTEEN CELLS OF THE TYPE
Hg-HgCl-satd. KCl/0.01 *M* HCl/0.10 *M* HCl/satd. KCl-HgCl-Hg

Time, hours	Av. pot., mv.	Av. dev., mv.
26	38.08	± 0.03
48	38.09	$\pm .05$
29	38.03	$\pm .03$
43	38.10	$\pm .04$
51	38.06	$\pm .06$
48	38.03	$\pm .07$
13	38.08	$\pm .03$
42	38.04	$\pm .05$
14	38.00	$\pm .04$
12	37.97	$\pm .03$
11	37.97	$\pm .02$
32	38.12	$\pm .01$
49	37.99	$\pm .07$
48	37.98	$\pm .04$

Av. 38.04

gives the number of hours during which readings were made on the respective cells; the second, the average potentials in mv. over the time interval indicated; the third, the averages of the deviations of the single readings from the average of each cell. The average potential of all the averages is 38.04 mv. The maximum deviation of this average potential from that for any one cell is 0.08 mv. and the mean of the average deviations is ± 0.04 mv.

Summary

1. An improved method for making a "free diffusion" type of static junction is described.

2. Static junctions of the type $0.1\ M\ \text{HCl/satd. KCl}$ or $0.01\ M\ \text{HCl/satd. KCl}$ must be made very definitely in order to be reproducible or constant, and when so made are constant for days to $\pm 0.04\ \text{mv.}$ average deviation, and reproducible to less than $0.1\ \text{mv.}$

3. The junction between 0.1 and $0.01\ M$ hydrochloric acid is constant and reproducible within the limits of dependability of the silver chloride electrodes used, or within $0.02\ \text{mv.}$

4. The potential of the cell system



commonly called the boundary potential between 0.01 and $0.10\ M$ hydrochloric acid has been determined to be $38.04 \pm 0.04\ \text{mv.}$ average deviation.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

LIQUID JUNCTION POTENTIALS. II. A DIRECT COMPARISON OF STATIC AND FLOWING JUNCTIONS¹

By ALFRED L. FERGUSON, KENNETH VAN LENTE AND RICHARD HITCHENS

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Many careful and extensive investigations during the last quarter century developed the general feeling that static liquid junctions are neither reproducible nor constant. This situation led to the development of the flowing junction.

Lamb and Larson,² who were the first to work extensively with the flowing junction, formed their junctions by allowing the more dense solution to flow up a vertical tube and meet the less dense solution flowing down, both then flowed out a common horizontal exit. This junction gave results constant and reproducible to one or two hundredths of a millivolt but the values were different from those which they obtained with static junctions. They also differed as much as 2.46 mv. from results obtained with another type of flowing junction apparatus which they used.

MacInnes and Yeh,³ with a modified form of the Lamb and Larson apparatus, showed that the potentials of cells containing solutions of the same concentration of a common ion varied with the rate of flow. They showed, also, that the potentials increase appreciably at low rates and decrease slightly at high rates of flow. Scatchard⁴ modified the apparatus used by MacInnes and Yeh in order to obtain an equal rate of

¹ The material presented in this article is from a portion of the thesis submitted to the Graduate School of the University of Michigan by Kenneth Van Lente in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Lamb and Larson, *THIS JOURNAL*, **42**, 229 (1920).

³ MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

⁴ Scatchard, *ibid.*, **47**, 696 (1925).

flow of the solutions. He also lengthened the horizontal part of the outlet tube to lessen the effects of mixing. His results with solutions of hydrochloric acid and saturated potassium chloride were reproducible and constant to a few hundredths mv. even with molal hydrochloric acid. He found that the potentials always rose when the flow was stopped, the maximum rise being 3.5 mv.

Other types of flowing junctions have been used by Aten and Van Dalfsen,⁵ by Roberts and Fenwick,⁶ and by Maclagan.⁷

It is evident from the literature that for a given piece of apparatus the flowing junction gives reproducible potentials at constant rates of flow but the values differ for different pieces of apparatus, and with the rate of flow, and do not agree with the values for static junctions.

The authors, in an earlier article, have described a method for obtaining highly reproducible and constant potentials for static junctions between saturated potassium chloride and different concentrations of hydrochloric acid. In the present work the apparatus was modified somewhat to make it possible to compare directly the potentials of static and flowing junctions.

Apparatus

Stopcock.—The stopcock which permitted the direct comparison of static and flowing junctions is shown in Fig. 1. A horizontal static junction may be made at the

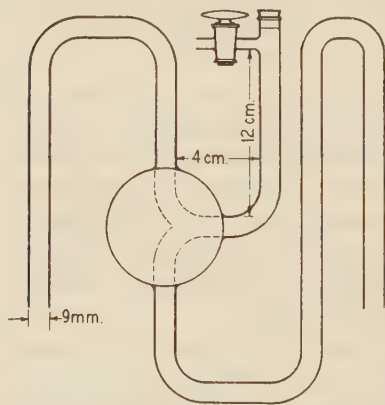


Fig. 1.—A diagram of a 9-mm. three-way stopcock which permitted the direct comparison of static and flowing junctions.

lower edge as described in the previous article. For the best results it is essential that the bore of the stopcock be exactly the same as that of the tubes leading to it. It was found necessary to have these made to order. The rate of flow was controlled by a stopcock in the exit tube. The small projection within the stopcock and opposite the outlet tube prevents the solutions from mixing when the junction is flowing. Preliminary experiments with sodium hydroxide solution on one side and water containing phenolphthalein on the other showed a very thin red ribbon-like layer which extended from the tip of the projection completely throughout the exit tube. This layer indicated that the junction was very thin at medium rates, somewhat mixed at high rates and diffuse at low rates of flow.

The measuring apparatus is the same as described in the previous article, except that the small dropping funnels were replaced with

those of 250-cc. capacity in order to supply sufficient solutions for the flowing junctions, thus making readjustment of the levels of the solutions infrequent.

⁵ Aten and Van Dalfsen, *Rec. trav. chim.*, **45**, 177 (1926).

⁶ Roberts and Fenwick, *THIS JOURNAL*, **49**, 2787 (1927).

⁷ Maclagan, *Biochem. J.*, **23**, 309 (1929).

Experimental

The first cell studied was the concentration cell



It consisted of two silver chloride electrode vessels with side arms dipping into beakers of the respective acid solutions. These two beakers were joined by one of the large stopcocks shown in Fig. 1, in which the liquid junction was made. The potentials of the static junctions were measured over periods of about twenty-five hours; then the static junctions were changed to flowing. The rate of flow was not changed in any case until the potential had become constant to 0.01 mv. for at least fifteen minutes.

In order to determine how much of the flowing junction was actually effective, the solutions in the outlet tube were stirred with a piece of fine rubber tubing. This stirring was started at the top of the vertical tube and continued until the solutions in the stopcock itself were mixed. The corresponding changes in potential were noted.

A summary of the results obtained with this concentration cell is given in Table I.

TABLE I

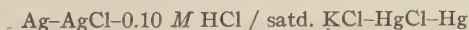
A COMPARISON OF THE VALUES OBTAINED WITH A CONCENTRATION CELL USING VARIOUS TYPES OF LIQUID JUNCTIONS

Cell no.	Static pot., mv.	Flowing pot.			Stopped flow pot., mv.	Stirred junct. pot., mv.
		Low 0.3 cc. per min.	Med. 1.0 cc. per min.	High 2.0 cc. per min.		
1	92.27	92.32	92.32	92.30	92.30	92.30
2	...	92.33	92.33	92.30	...	...
3	92.27	92.32	92.30	92.30	92.30	92.30
4	...	92.32	92.30	92.31	92.30	92.30

It may be seen from Table I that the type of junction in a concentration cell makes practically no difference in the potential. These results confirm those obtained by Scatchard and Buehrer⁸ with somewhat similar systems.

In these experiments the electrodes remained constant in potential to 0.02 mv. for periods longer than the cells were studied.

The next junction studied was that contained in the cell



It was made in a manner similar to the one just described. In this case it was necessary, however, to adjust the solutions to the same hydrostatic pressure. Leaks in these cells were found especially troublesome when the junctions were flowed and all places had to be absolutely air-tight. The importance of keeping the potassium chloride solution saturated, as pointed out by Scatchard,⁴ was observed here and to ensure this, crystals of potassium chloride were kept in the lower tube leading to the stopcock. Three

⁸ Scatchard and Buehrer, *THIS JOURNAL*, 53, 574 (1931).

cells were measured first with static and then with flowing junctions. The average potentials of the three static junctions were 44.76, 44.76 and 44.75 mv., respectively, with a mean average deviation over forty-eight hours of ± 0.02 mv. The results obtained with the flowing junction are represented graphically in Fig. 2.

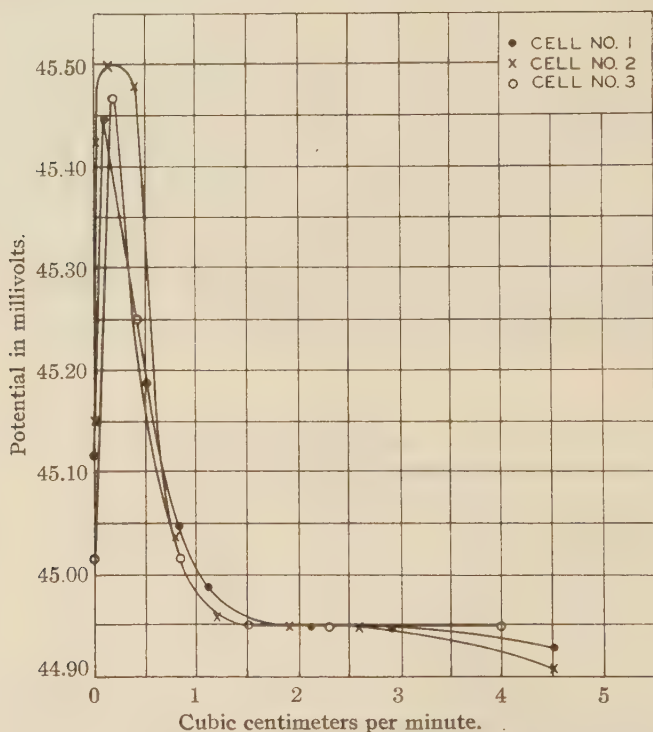


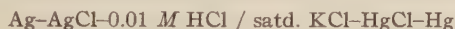
Fig. 2.—Curves showing the variations with the rate of flow of the potentials of the cells Ag—AgCl—0.10 *M* HCl/satd. KCl—HgCl—Hg.

It is evident, immediately, that the potentials vary greatly with the rate of flow and rise to a maximum at low rates. This maximum could be reproduced to 0.05 mv. and could be approached equally well from either direction. The potentials always decreased from the maximum when the flow was stopped, to values which might differ in separate experiments by 0.1 mv. and which were, on an average, about 0.1 mv. higher than the constant value at moderate rates. With rates of flow from 1.5 to 3.5 cc./min. the potentials were constant and reproducible in the different cells to 0.01 mv. For rates of flow greater than 3.5 cc./min. there was a slight decrease in potential. The constant potential obtained at medium rates of flow was about 0.2 mv. higher than the equally constant and reproducible value for the static junction obtained with identically the

same system before the flow was started. The shape of the curves was the same whether the rate of flow was varied from low to high or from high to low rates of flow.

Stirring the solutions in the outlet tube had no effect upon the potential until a point within 3 cm. of the stopcock itself was reached. From this point on the effect became greater until a maximum drop of 1.5 mv. was observed, when the solutions in the stopcock itself were completely mixed. This shows that the effective part of the junction is about the first 3 cm. of the horizontal tube.

The third junction studied was that in the cell



which is identical with the previous cell except for the concentration of the acid solution. Three cells of this type were run with static and flowing junctions. The averages of the three cells with static junctions were 99.04, 99.14 and 99.16 mv., respectively, with a mean average deviation of ± 0.03 mv. for forty-eight hours. The potentials of the cells with flowing junctions are represented graphically in Fig. 3.

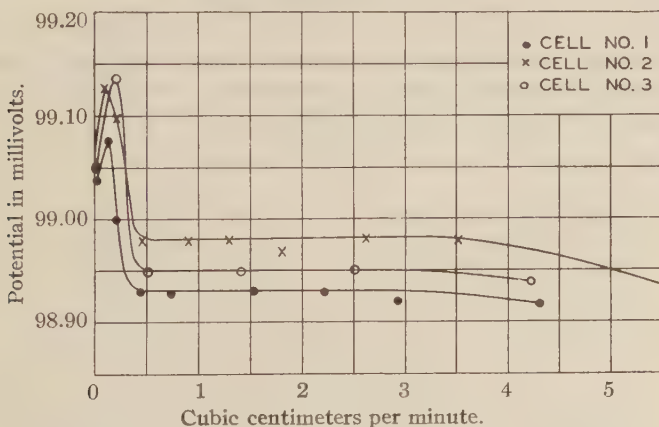


Fig. 3.—Curves showing the variations with the rate of flow of the potentials of the cells Ag-AgCl-0.01 *M* HCl/satd. KCl-HgCl-Hg.

In many respects the behavior of this junction is similar to the previous one, but in some respects it is distinctly different. There is an increase in potential at low rates and a slight decrease at high rates of flow. The values at medium rates are just as constant but less reproducible than those obtained with 0.10 *M* acid. There is also a decrease from the maximum when the flow is stopped, to a value about 0.1 mv. higher than that at medium rates of flow. When stirred, however, the junction with 0.01 *M* solution increased in potential 0.3 mv., while the 0.1 *M* decreased 1.5 mv.; also, with the 0.01 *M* solution the value at medium rates of flow

was 0.15 mv. lower than the average potential of the static junctions, while with the 0.10 *M* solution it was 0.2 mv. higher. These results indicate that saturated potassium chloride does not eliminate the boundary potential against hydrochloric acid solutions, that the remaining potential is different for different concentrations, and that it cannot be assumed that boundaries of different concentrations will respond in the same manner to disturbing influences.

Summary

1. An apparatus has been developed for the direct comparison of static, flowing, "stopped flowing," and stirred junctions.
2. For concentration cells of 0.10 *M* and 0.01 *M* hydrochloric acid the potential is practically the same for all these types of junction.
3. For the junctions 0.10 *M* HCl / satd. KCl and 0.01 *M* HCl / satd. KCl the potential in each case depends upon the type of junction and the rate of flow, but these two junctions respond in opposite ways to certain treatments.
4. The effective part of this type of flowing junction is that contained in the first three cm. of the horizontal outlet tube.
5. For the systems involving saturated potassium chloride, the potentials with static junction are less empirical than those with flowing, because the variations of the potentials of the former with time are less than the variations of the latter with rate of flow.

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High-Precision Constant-Temperature Bath

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RICHARD HITCHENS

University of Michigan, Ann Arbor, Mich.

THE temperature-control system herein described is the culmination of developments in this laboratory which have extended over the last 20 years. The objective has been to construct a system such that every part would function continuously without attention over a period of many months and maintain a temperature constant throughout the whole period to less than 0.01°C . maximum variation, and which would operate over shorter periods to within 0.001°C . Those who have had occasion to maintain accurate temperature control over long periods of time are familiar with various exasperating factors, such as breaking of belts, fluctuation of temperature of room or of the cooling water, sticking of relay contacts, fouling of regulator contacts, failure of dry cells or storage batteries, burning out of heating elements, electrical leaks, lags in the controlling system, gradual creeping of temperature, etc. The system described has been in use now for about 2 years and during that period has remained free from these disturbing factors.

A satisfactory thermostat must consist of a suitable container, well insulated thermally. The bath liquid should be transparent, nonvolatile, of low viscosity and electrical conductivity, but of high specific heat. The stirring apparatus must keep all parts of the bath at the same temperature. The cooling and heating systems must take care of all fluctuations in room temperature with no time lag. The thermoregulator and control system must respond instantly to minute temperature changes, must not be affected by outside

factors, must be automatic, and must not require readjustment.

The essential parts of the apparatus are represented in Figure 1. The bath liquid is petrolatum, an odorless, transparent mineral oil of fairly low viscosity and low electrical conductivity. A variable external resistance allows adjustment of the heating current.

The efficiency of stirring is appreciably increased by a

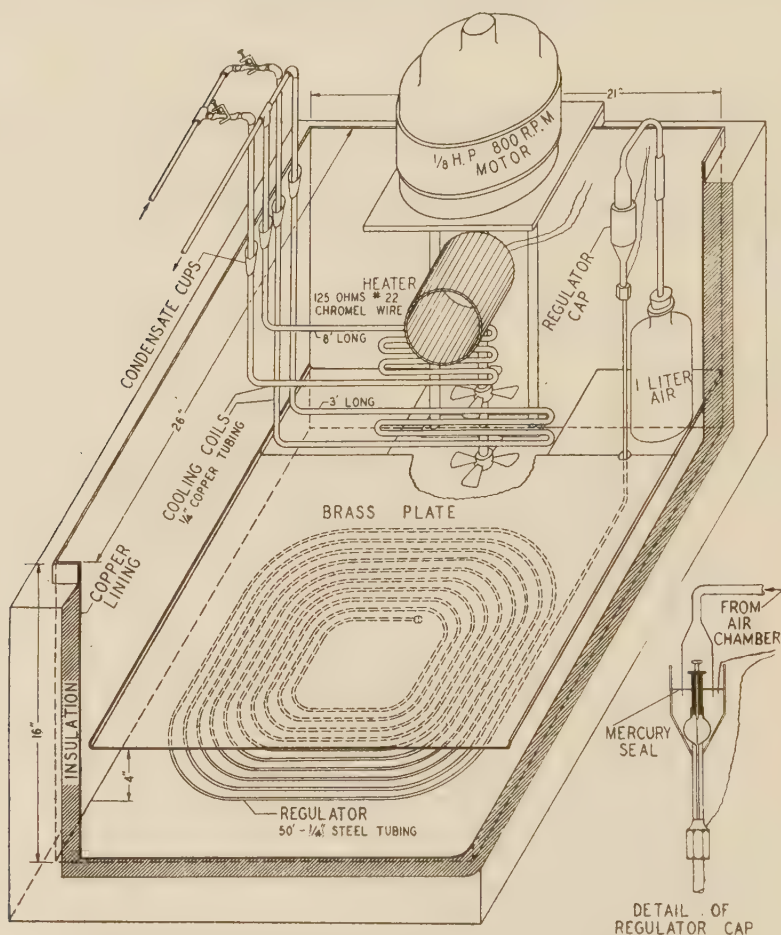


FIGURE 1. DIAGRAM OF APPARATUS

metal plate mounted as indicated. The oil makes a complete circuit in from 10 to 15 seconds. This system keeps the temperature of all parts of the bath the same within the limits of reading a Bechmann thermometer.

Although the relative coefficient of expansion of mercury in steel is much smaller than that of toluene in glass, which

is another widely used type of regulator, yet the much higher heat conductivity and lower specific heat of mercury and of steel, and the thin wall of the steel tubing make the mercury regulator the more desirable. The large surface of thin-walled metal tubing reduces time lag to a negligible quantity.

The regulator was filled slowly under a high vacuum. The upper end was fastened to a vacuum oil pump, and the lower end, fitted with a metal cap through which an extremely small hole had been drilled, was placed under mercury. It was insulated from the bottom of the bath by glass cups. The top of the regulator terminates in a glass capillary tube cemented to the steel tube and fitted with a metal cap through which passes a thin steel machine screw of extremely fine thread. This steel pin makes contact with the mercury just at the point where the glass capillary opens into a small bulb.

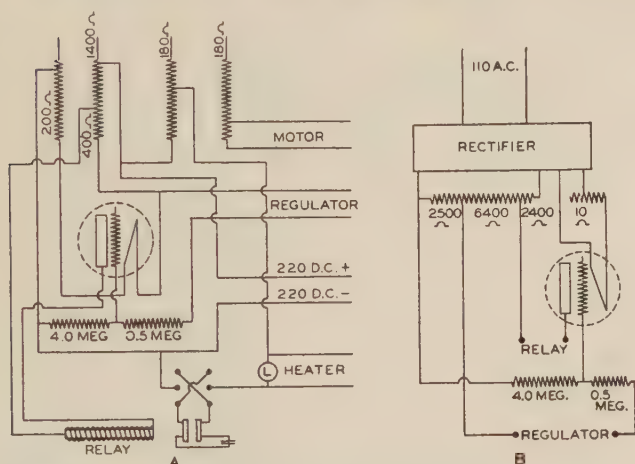


FIGURE 2. WIRING DIAGRAMS EMPLOYING 220 VOLTS D. C. AND 110 VOLTS A. C., RESPECTIVELY

It appears to be impossible to remove the last traces of air from the regulator. When the thermostat was first operated, a correlation was observed between barometric pressure and temperature of the bath. To eliminate this disturbing factor an arrangement was constructed to keep the mercury surface in the regulator under nearly constant pressure. A 1-liter bottle filled with air was placed in the constant-temperature bath. This was connected through a capillary tube to a wider tube which fitted over the regulator top and into a mercury seal, as shown in the detail drawing. Changes in barometric pressure produce practically no change in pressure within the bottle and thus upon the mercury in the regulator. This device eliminates entirely the influence of changes in barometric pressure.

Automatic control is accomplished by the use of the vacuum tube set-up of Beaver (1) adapted to the X'71A tube. Since

in this system only 10 microamperes flow through the regulator, there is no sparking and thus no oxidation of the mercury surface.

The X '71A tube is well adapted for this purpose since, with a filament current of only 0.20 ampere, zero grid potential, and 75 volts plate potential, a plate current of 12 milliamperes, which is much more than is required to operate the relay, is produced. A negative grid potential of 25 volts reduces the

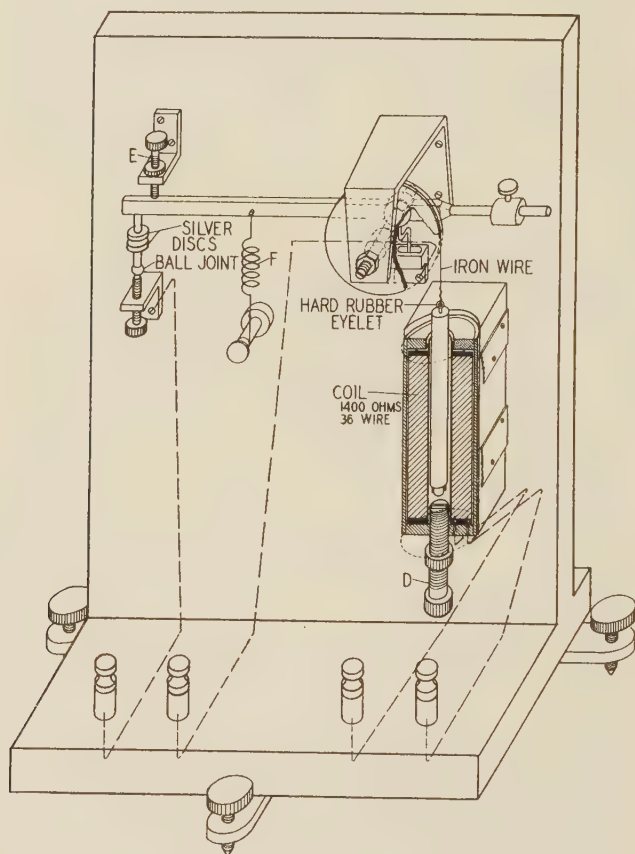


FIGURE 3. DIAGRAM OF RELAY

plate current to zero, an absolutely essential feature. Two X '71A tubes on separate thermostats have been in constant use for 18 months with little sign of deterioration.

Two wiring diagrams are shown in Figure 2. System A employs 220 volts d. c. and is a modified form of the one described by Beaver. It will be seen that 110 volts d. c. could be used equally well. System B uses 110 volts a. c. in conjunction with a radio A. B. C. power pack which contains

an X '80 full wave-rectifier tube. Both systems have been in use interchangeably with equal satisfaction.

The essential features of the relay used are represented in Figure 3. The soft-iron core of the electromagnet is covered with thin paper to prevent sticking to the thin brass tube upon which the wire is wound. The bottom of the plunger is cut away as shown, and the depression filled with several layers of paper to prevent sticking at the lower edge. Adjustment is made by means of the soft-iron set screw *D* in the bottom of the electromagnet, the stop *E*, the adjustable spring *F*, and the counterbalance weight.

The relay is extremely sensitive. With a coarse adjustment it operates over a range of from 7 to 25 milliamperes, but can readily be made to operate over a range of from 2 to 12 milliamperes.

The system is so sensitive that the relay operates with a

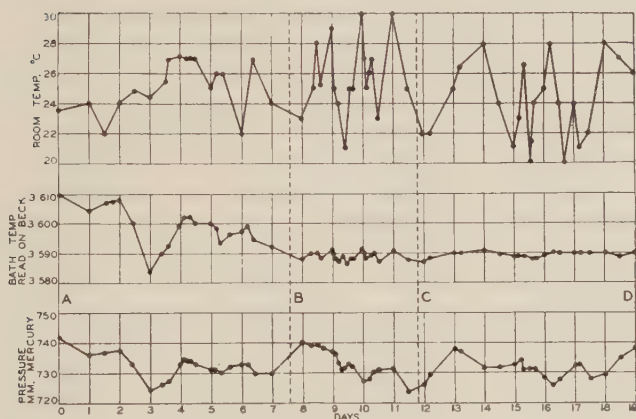


FIGURE 4. BATH TEMPERATURE *vs.* BAROMETRIC PRESSURE BEFORE AND AFTER APPLICATION OF CONSTANT-PRESSURE DEVICE, AND BATH TEMPERATURE *vs.* ROOM TEMPERATURE

continuous chatter. This can be prevented by means of a small condenser across the 4-megohm resistance in Figure 2. A 0.02-mf. condenser causes the relay to operate about once a second. The reliability of the instrument is demonstrated by the fact that one has been used continuously for more than a year without a single adjustment.

When the thermostat was first operated, a record was made of room temperature, barometric pressure, and thermostat temperature. The results are represented graphically in Figure 4. The lower curve shows the fluctuations in pressure, the center one fluctuations in thermostat temperature, and the upper one the changes in room temperature. The correlation between thermostat temperature and barometric pressure is evident over the portion of the curve from *A* to *B*. At the point *B* the constant-pressure device was attached. It will be

observed that this eliminated the influence of pressure. From *B* to *C*, however, there is a slight change in thermostat temperature with room temperature. At the point *C* the rate of heating and cooling was increased. This eliminated the influence of changes in room temperature. Under these conditions the temperature of the bath can be held constant for days within the limits of error of reading a Bechmann thermometer. Since, however, such accurate temperature control is usually not necessary, the customary operating conditions are best represented by the center section of the curves.

LITERATURE CITED

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